

Modeling the observations of in vivo bubble formation with hydrophobic crevices

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Tikuisis P. Modeling the observations of in vivo bubble formation with hydrophobic crevices. *Undersea Biomed Res* 1986; 13(2):165-180.—In vivo hydrophobic crevices from which bubbles emerge upon decompression are hypothesized to account for experimental observations of bubble formation in decompressed shrimp. The conical crevice model can be used to explain the sharp increase in the number of bubbles observed in shrimp for decompression ratios greater than 4:1. In accordance with the observed attenuating effects of pressure pretreatment on bubble formation in shrimp, the model can also be used to explain: (a) the evolution of the gas nuclei to smaller stable sizes during compression; (b) the return of the nuclei to their original stable configurations when the overpressure is removed; and (c) the requirement for greater decompressions to cause emergence of bubbles from the nuclei as the magnitude and period of pressure pretreatment are increased. A new crevice geometry with elliptically shaped walls is introduced which reduces the height of the crevice needed for bubble emergence and relaxes the constraints for the stability of gas nuclei. This new geometry reduces the height of crevices required for the prediction of bubble emergence an order of magnitude when compared to the conical crevice, and satisfies the hydrophobic crevice condition as long as the crevice surface has a contact angle greater than 90° .

gas nuclei
bubble formation

hydrophobic crevice
decompression

shrimp

Decompression sickness is the result of the formation of gas bubbles in the body. Vertebrates are more susceptible to bubble formation than are microorganisms. For example, a gas supersaturation of 78.0 kPa (0.77 atm) is sufficient to produce venous gas bubbles in human subjects when decompressed from saturation depth to atmospheric pressure (1). Less developed organisms have greater resistance to bubble formation; in fact, the gas supersaturation required to produce N_2 bubbles in unicellular microorganisms exceeds 17.2 MPa (170 atm) (2). The mechanism of bubble formation in all bodies, when subjected to a decompression stress, is a topic of some controversy.

According to homogenous nucleation theory, a gas supersaturation in excess of 100 MPa is necessary for the de novo formation of gas bubbles in the bulk liquid of

weak liquid-gas solutions such as N_2 in water at room temperature and pressure (3). Yet gas bubbles have nucleated at the interface of glass and liquid in a N_2 -water solution, saturated at above 16.2 MPa and at 298°K, and then decompressed to ambient pressure (4). Such spontaneous heterogeneous nucleation may explain the mechanism of de novo bubble formation in microorganisms, but not in vertebrates unless the liquid surface tension is reduced, for example, to a value of less than 0.005 N/m (5). However, aside from lung surfactant, fluids with such low surface tensions have not been identified in the body; therefore other mechanisms of bubble formation in vertebrates must be considered.

Gas bubbles can be produced by the mechanism of tribonucleation (6). When two solid surfaces immersed in a liquid make contact and break away, bubbles may form depending on the viscosity of the liquid, the velocity of the separation of the surfaces, and the concentrations and solubilities of gases dissolved in the liquid. Bubbles have formed along the path of contact of a rolling ball in a glass container of a N_2 -olive oil solution saturated at 101.3 kPa (1 atm) and at 298°K, and decompressed by 16.2 kPa (7). Tribonucleation is thought to occur in many locations in the body (7), at joint surfaces, in blood vessels undergoing collapse and expansion, and at muscle tendon inserts.

The very low level of gas supersaturation necessary for bubble formation makes tribonucleation a prime candidate for the mechanism of bubble formation in vertebrates. Indeed, this is the conclusion of McDonough and Hemmingsen (8) in their observation of bubble formation in some crustaceans. However, not all bubble formation in the crustaceans can be explained by tribonucleation. For instance, the susceptibility to bubble formation in the lumen of the gut of the brine shrimp, *Artemia*, is reduced by pressure pretreatment (8), i.e., when a large hydrostatic stress is applied for a short time before exposure at a lower pressure. Pressure pretreatment should enhance, not reduce, the rate of bubble formation by tribonucleation, since this treatment can only add to the gas saturation of the liquid-gas solution. The effect of increasing resistance to bubble formation by pressure pretreatment has also been reported by Daniels et al. (9) in the common shrimp, *Crangon crangon*. To explain this effect, the premise is made in this study for the existence of gas nuclei that are stabilized under normal conditions but are susceptible to shrinkage or collapse with pressure pretreatment.

Under normal conditions, living tissue is undersaturated with inert gas (10). A gas bubble in an undersaturated liquid-gas solution will dissolve away unless; (a) the liquid contains stabilizing molecules (11), (b) the liquid is closed to external gas transfer and is of sufficiently small volume or contains a sufficient number of bubbles (12), and/or (c) the bubble is contained in a hydrophobic crevice (13). There is in vitro experimental evidence to support all three of these mechanisms of nuclei stabilization. However, it is not clear how the gas nuclei, pertaining to the first two mechanisms of stabilization, are produced in vivo.

A gas nucleus will form spontaneously in a hydrophobic crevice, i.e., where the liquid-gas interface is concave to the liquid, as shown in Fig. 1, and remain stable for undersaturated conditions (14). In this paper it is shown that, under certain assumed conditions, the hydrophobic conical crevice model can account for the existence of gas nuclei and their emergence in decompressed shrimp with and without pressure pretreatment. Although the conical crevice model can explain the observed results, to do so a very long, narrow crevice must be postulated. In addition, certain con-

straints to meet the hydrophobic condition must be applied to ensure stability of nuclei. A different, more realistic, crevice shape is introduced which both reduces the height of the crevice and relaxes the constraints for nuclei stability.

BACKGROUND

Hydrophobic condition

Certain restrictions on the value of the contact angle, θ , must be met to satisfy the hydrophobic crevice condition. The contact angle is the angle subtended between the solid-liquid and the liquid-gas interfaces as measured through the liquid (Fig. 1). For a surface that is hydrophobic, θ must exceed 90° , whereas for a crevice that is hydrophobic, θ must exceed 90° by an amount that depends on the crevice geometry.

At this time, one cannot point to the source of large contact angles in the body; however, many of the bubble observations are explainable with this condition. Therefore, it is worthwhile to show the correspondence between the observation of bubbles in decompressed shrimp and the prediction of bubble formation with hydrophobic crevices.

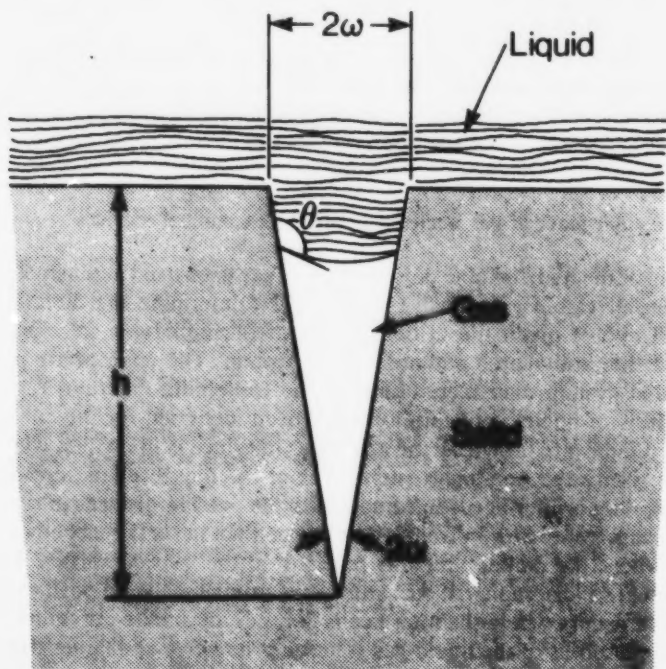


Fig. 1. Schematic of the conical crevice model where h is the height of the crevice, ω is the radius of the crevice mouth opening, 2α is the apex angle, and θ is the contact angle subtended between the solid-liquid and liquid-gas interfaces as measured through the liquid.

Critical radius

The critical radius of a liquid-gas solution, R_c , is defined as (3)

$$R_c = 2\gamma/(\eta P_v + \sum_{i=1}^n c_i K_{Hi}/c_o - P_L), \quad (1)$$

where γ is the surface tension of the liquid-gas solution, P_v is the vapor pressure of the pure liquid across a flat interface; η is the correction factor to account for the curvature of the interface; c_i is the concentration of the i^{th} component of the dissolved gas; K_{Hi} is the Henry's coefficient of solubility of the i^{th} gas component in the liquid; c_o is the density of the pure liquid; and P_L is the liquid pressure. Since the parameters of the critical radius are properties of the liquid-gas solution, the critical radius itself is also a property of the solution, whether or not a bubble is present (15). When the interfacial radius of curvature of a gas nucleus has the same value as the critical radius, then the nucleus is in equilibrium with the liquid-gas solution.

In the present study, the deviation of η from unity is negligible and therefore is neglected. The vapor pressure of the physiological fluid will be assumed to have the value of saturated water vapor pressure at the temperature of the physiological body. The summation term in eq. 1 represents the total gas tension of inert and metabolic gases, Π , dissolved in the fluid. Finally, the pressure in the fluid will be assumed to be equal to the value of the ambient pressure, P_a . Therefore, the critical radius of the physiological fluid can be expressed as

$$R_c = 2\gamma/(P_v + \Pi - P_a). \quad (2)$$

Note that the critical radius can assume both negative and positive values depending on whether the sum of the vapor pressure and total gas tension is smaller or larger than the ambient pressure. These conditions occur when an equilibrated liquid-gas solution is compressed or decompressed, respectively.

Stability and emergence of gas nuclei in hydrophobic conical crevices

The model of the hydrophobic conical crevice has been used extensively to explain the existence of stable gas nuclei (13,16,17). To determine the direction that the nucleus will evolve given the critical radius of the liquid-gas solution, one must examine the thermodynamic potential of the system. The appropriate potential for an unbounded system, considered here, is the Helmholtz function, F , (14). Three distinct regions of nuclei configuration have been identified for the conical crevice (18). These regions are (a) where the liquid-gas interface is in contact with the inside surface, (b) where the liquid-gas interface is at the mouth of the crevice, and (c) where the liquid-gas interface is in contact with the outside surface. In region (b), the interface undergoes a rotation from where the contact angle is reached on the inside surface to where the contact angle is reached on the outside surface. During this rotation, the interfacial radius of curvature goes from negative to positive values and this transition occurs where the interface is flat, i.e., of infinite curvature.

If the critical radius of the liquid-gas solution is negative and larger than the value $\omega/\cos(\theta-\alpha)$ where ω and α are defined in Fig. 1, then a single equilibrium state is found in region (a) where the liquid-gas interface has negative curvature, as shown in Fig. 1. Following the methods outlined in (14) and using the expressions developed for the conical crevice in (18), the Helmholtz function for virtual equilibrium states about this point was calculated and is shown for one particular set of conditions in Fig. 2a. A true equilibrium state is where F is an extremum. Since the extremum in this case has a minimum value, the equilibrium state here is a stable one. Thus, a gas nucleus in the crevice will evolve to this state and remain there.

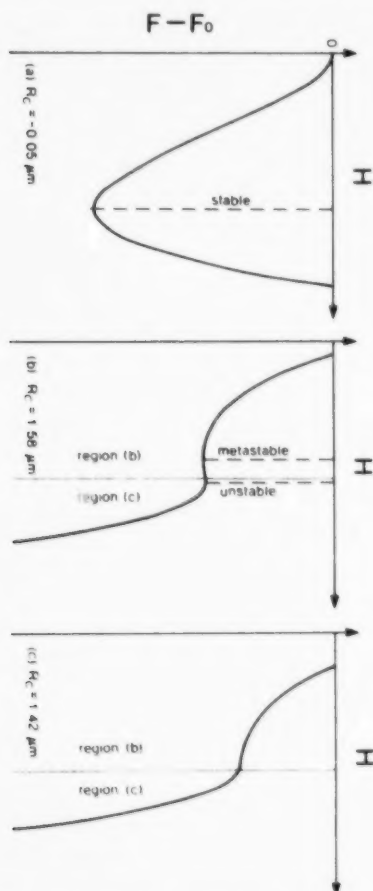


Fig. 2. Change in the Helmholtz function, $F - F_0$ where F_0 is the Helmholtz function for the homogeneous system, plotted against the height of the gas nucleus, H , as measured from the apex of the conical crevice ($\theta = 95^\circ$, $\alpha = 2^\circ$, $h = 42.8 \mu\text{m}$) for $R_c = -0.05$, 1.58 , and $1.42 \mu\text{m}$. These values of the critical radius correspond to an inert gas tension of 98.8 kPa , a temperature of 294°K , and to liquid pressures of 2.53 MPa , 25.3 Pa , and 12.7 Pa , respectively. Minimum value of F in *a* occurs in region *a* at $H = 0.075 \mu\text{m}$, and the local minimum and maximum values of F in *b* occur in region *b* at $H = 43.87 \mu\text{m}$ and in region *c* at $H = 44.24 \mu\text{m}$, respectively. Transition from region *a* to region *b* occurs at $H = 42.76 \mu\text{m}$ and transition from region *b* to region *c* occurs at $H = 44.17 \mu\text{m}$.

If the critical radius of the liquid-gas solution has a value between $\omega/\cos(\theta-\alpha)$ and $-\infty$, then a single equilibrium state is found in region (b) where the liquid-gas interface has negative curvature. This equilibrium state is also stable. If the critical radius has a value between ∞ (the transition between $-\infty$ and $+\infty$ occurs when the liquid-gas interface is flat) and $\omega/\sin\theta$, then there are two equilibrium states for the system. One state is found in region (b) where the liquid-gas interface has positive curvature, i.e., convex to the liquid, and the other state is found in region (c). These equilibrium states are shown in Fig. 2b where the local minimum value of F occurs in region (b)

and where the local maximum value of F occurs in region (c). A gas nucleus in the equilibrium state with the local minimum value of F is of smaller size and metastable and one in the equilibrium state with the local maximum value of F is of larger size and unstable. Therefore, a gas nucleus of size smaller than that of the unstable state will evolve to the metastable state and tend to stay there. Note that this can occur even if the nucleus is in region (c). If the nucleus is of size larger than that of the unstable state, then it will grow without bound.

If the critical radius of the liquid-gas solution is positive and less than the value $\omega/\sin\theta$, then there is no equilibrium state for the gas nucleus in the conical crevice. Physically, this means that during the growth of the gas nucleus its positive interfacial radius of curvature can never become less in value than the critical radius. This is depicted in Fig. 2c where F decreases monotonically with increasing size of the gas nucleus. In this instance, the gas nucleus will also grow without bound.

If the critical radius of the liquid-gas solution is equal to the value $\omega/\sin\theta$, then a single equilibrium state exists and it is found at the transition between regions (b) and (c). However, this state is unstable since the Helmholtz function has an inflexion at this equilibrium point and a slight perturbation will cause the gas nucleus in this state to evolve away from it and grow without bound. Therefore, this state represents the minimum condition necessary for the gas nucleus to grow out of the crevice. To assure growth, no equilibrium state must exist for the system, thus the critical radius of the liquid-gas solution must be positive and of value less than $\omega/\sin\theta$. This value will be denoted as R_m . R_m physically represents the positive minimum value of the interfacial radius of curvature that the nucleus must pass through to evolve from the hydrophobic conical crevice. The conditions for which R_c is less than R_m for the conical crevice will be examined in the next section.

The emergence of the nucleate bubble ultimately depends on the size required to detach from the crevice site. The mechanism of detachment of the bubble nucleate from the crevice site is beyond the scope of this paper. The concern here is only with the prediction of the direction that the nucleus will evolve given its initial size and the critical radius of the liquid-gas solution. If the conditions for unbounded growth are satisfied, such as that shown in Fig. 2c, then the nucleus becomes a candidate for emerging as a bubble.

CONICAL CREVICE MODEL

In the experiments of Daniels et al. (9), bubbles readily formed in the shrimp when decompressed from the surface to a pressure of 10.1 kPa. This represents a decompression ratio of 10:1. If one assumes for the shrimp a value of the liquid surface tension of 0.060 N/m and a combined initial value of the vapor pressure and total gas tension of 101.3 kPa, then the critical radius is 1.32 μm at the decompressed level of 10.1 kPa. For gas nuclei to grow in the decompressed shrimp under these conditions, the value of R_m must be larger than 1.32 μm . If one chooses for the conical crevice model a crevice height of 42.8 μm , a half-apex angle of 2° , and a contact angle of 95° , then the value of R_m is 1.5 μm . These are the parameters of the conical crevice that will be used to examine the experimental data of Daniels et al. (9) on the decompression of the shrimp.

The initial state of gas saturation in the shrimp is not known. If, as assumed above, the combined initial value of the vapor pressure and the total gas tension is 101.3 kPa, then the initial value of the critical radius, according to eq. 2, is infinite. For modeling purposes, it is not essential to know the precise initial condition since the prediction of stability and emergence of the gas nucleus can be made approximately the same for a range of initial conditions by adjusting the crevice characteristics. To satisfy the crevice characteristics given above, the assumed initial condition of infinite critical radius is one in which the crevice is completely filled with gas and the liquid-gas interface is flat at the mouth of the crevice. Therefore, the initial assumed value of the total gas tension, i.e., the difference between Π and P_a , at a temperature of 294°K (temperature used in the shrimp experiments) is 98.8 kPa.

Normal decompression

Daniels et al. (9) exposed shrimp to various near instantaneous altitude decompressions and recorded the mean bubble count in each case. In this study, the conical crevice model is subjected to the same altitude decompressions and the predictions for bubble emergence are then compared to the mean bubble count that was found in the shrimp.

The first three columns of Table 1 give the decompression ratio applied to both the crevice model and to the shrimp, the mean bubble count (MBC) in the shrimp, and the corresponding ambient pressure, P_a . The next column gives the radius of curvature of the liquid-gas interface of the gas nucleus immediately after decompression, $R(0^+)$. This was determined by using the ideal gas equation. It was assumed that during the almost instantaneous decompression, the nucleus changed size isothermally and that there was no gas transfer in to or out of the nucleus. When this procedure was applied to the various conditions of decompression, the values of the radii of curvature became positive, indicating that the nuclei had expanded out of the crevice. The corresponding height of the nucleus, H , as measured from the apex of the crevice, is

TABLE 1
MEAN BUBBLE COUNT $\pm$ SEM IN DECOMPRESSED SHRIMP^a AND THE PREDICTED GROWTH OF NUCLEI IN THE CONICAL CREVICE MODEL FOR VARIOUS DECOMPRESSION RATIOS

Decompression Ratio	MBC $\pm$ SEM	P_a , kPa	$R(0^+)$, μm	$H(0^+)$, μm	$R_c(0^+)$, μm
1.5:1	0.1 $\pm$ 0.1	67.6	3.68	43.12	3.56 ^c
2:1	0.3 $\pm$ 0.2	50.7	2.46	43.31	2.37 ^c
4:1	0.5 $\pm$ 0.3	25.3	1.66	43.74	1.58 ^c
6:1	3.2 $\pm$ 0.5	16.9	1.52	44.04	1.42
8:1	3.7 $\pm$ 1.9	12.7	4.54 ^b	46.94	1.35
10:1	3.6 $\pm$ 0.8	10.1	4.82 ^b	47.20	1.32
12:1	4.6 $\pm$ 0.8	8.4	5.03 ^b	47.39	1.29

^aSee reference 9; ^bvalue attained if still attached to the crevice; ^cmetastable equilibrium state.

given in the fifth column of Table 1. The last column of Table 1 gives the value of the critical radius, $R_c(0^-)$, of the liquid-gas solution immediately after the decompression.

The mean bubble count in shrimp was less than unity for decompression ratios of 4:1 or less (Table 1). For ratios larger than this, the mean bubble count increased about an order of magnitude indicating that a threshold for significant bubble formation had been reached. For the conical crevice model, metastable equilibrium states exist for decompression ratios of 4:1 or less. (Fig. 2*b*, in fact, shows the Helmholtz function for the conditions considered here and for a decompression ratio of 4:1.) Note that for these low decompressions, the nuclei are found in region (b) and therefore one predicts from this model that the nuclei will evolve to the corresponding metastable equilibrium states and not emerge from the crevice. For example, in the case of the 4:1 decompression, the height of the nucleus begins at 43.74 μm (Table 1) and therefore the nucleus is to the left of the metastable state shown in Fig. 2*b*. Thus the nucleus will grow until its height reaches 43.87 μm and no further growth will take place.

Although some bubbles do emerge in the shrimp for these low decompression ratios, this does not invalidate the crevice model since a crevice of slightly different dimensions will produce bubbles under these conditions. For example, wider crevice mouth openings will have larger R_m values from which bubbles can emerge under a condition of less gas supersaturation or larger R_c value. Therefore a distribution of sizes could be used to explain the bubble observations in the decompressed shrimp for the full range of decompression ratios. As will be seen, however, the threshold increase in bubble formation that is observed in the shrimp when the decompression ratio exceeds 4:1 suggests that the majority of bubble sites behave as the model that is described herein.

For a decompression ratio of 6:1, the interfacial radius of curvature, R , of the gas nucleus in the conical crevice is 1.52 μm immediately after decompression and the corresponding height of the nucleus is 44.04 μm (Table 1). The critical radius following this decompression is 1.42 μm and no equilibrium state exists for the system, as shown in Fig. 2*c*. Growth, therefore, is thermodynamically favorable but its rate is limited by the kinetic effect of the diffusion of gas through the liquid, which lowers the gradient for gas transfer into the nucleus. Furthermore, the thermodynamic state of the system may change due to the depletion of gas in the liquid to the surrounding low pressure environment. This would lead to a decreasing gas tension and therefore an increasing value of R_c . If the value of R reaches R_m before the value of R_c reaches R_m , then the nucleus will continue to grow. This is likely in the present circumstance of a 6:1 decompression ratio since the value of $R(0^-)$ is very close to R_m .

For decompression ratios of 8:1 and greater, the nucleus expands beyond the R_m value of 1.50 μm during the decompression and therefore it will grow. The rate of this growth, although limited by the effects of gas diffusion and gas depletion in the liquid, is increased with greater decompression stress since the gradient for gas transfer from the liquid into the nucleus is also increased. Therefore bubble emergence becomes increasingly probable with increased decompression stress. This prediction is consistent with the trend of increasing mean bubble counts in the shrimp as the decompression ratio is increased (9).

Decompression with pressure pretreatment

Daniels et al. (9) found that the mean bubble counts in shrimp decreased when pressure pretreatment to 2.53 MPa (25 atm) was applied before decompression to

10.1 kPa. The mean bubble counts were 2.6, 2.2, and 0.7 for pressure pretreatment periods of 10, 120, and 600 s, respectively. In Table 2, the interfacial radii of curvature and the corresponding heights of the nuclei are given for the conical crevice model at (a) the end of the pressure pretreatment period, (b) upon return to surface (i.e., at 101.3 kPa), and (c) immediately following decompression to 10.1 kPa. These values are given for three different pretreatment periods; at 0⁺ corresponding to an instantaneous pressure spike, and at two arbitrarily chosen times, t_1 and t_2 . The gas tension during decompression is assumed to be unchanged from its initial value of 98.8 kPa. This closely approximates the experimental conditions since the shrimps were placed in plastic bags that transmitted the pretreatment pressure but not the inert gas. The shrimp were then removed from the bags after returning to surface conditions.

When the pressure spike is applied to the conical crevice model and no gas transfer takes place, the gas nucleus returns to its original state upon return to surface. When decompressed further to 10.1 kPa, spontaneous growth is predicted as if no pressure pretreatment were applied (Table 1). The observation of a mean ($\pm$ SEM) bubble count of 2.6 ± 0.8 in the shrimp, after decompression to 10.1 kPa following 10 s of pressure pretreatment at 2.53 MPa, is in close agreement with the model prediction of no change from the case where no pressure pretreatment was applied.

In the case where the pretreatment pressure is applied for a finite period of time, the interfacial radius of curvature of the conical crevice begins at $-9.71 \mu\text{m}$ (Table 2). Since the critical radius is $-0.05 \mu\text{m}$, corresponding to a gas tension of 98.8 kPa, a gradient for the transfer of gas out of the nucleus is established and, in time, the nucleus diminishes in size. Critical radii of negative values represent stable equilibrium states for the hydrophobic crevice,¹ as shown in Fig. 2a. Therefore, as the nucleus evolves toward the new equilibrium state, its interfacial radius of curvature evolves to smaller negative values and the height of the nucleus becomes smaller.

TABLE 2
PREDICTION OF NUCLEI EVOLUTION IN THE CONICAL CREVICE MODEL DURING
PRESSURE PRETREATMENT AT 2.53 MPa, UPON RETURN TO SURFACE, AND
FOLLOWING DECOMPRESSION

Period of Pressure Pretreatment	Evolution of Nuclei					
	At End of Pressure Pretreatment Period		At Return to Surface, 101.3 kPa		Following Decompression to 10.1 kPa	
	$R_c = 0.05 \mu\text{m}$		$R_c = \infty$		$R_c = 1.32 \mu\text{m}$	
	R, μm	H, μm	R, μm	H, μm	R, μm	H, μm
0 ⁺	-9.71	14.54	∞	42.80	4.82*	47.20
t_1	-5.00	7.49	-15.0	22.46	20.8	42.85
t_2	-1.00	1.50	-3.37	5.05	-16.8	22.16

*Value attained if still attached to crevice.

¹Because of this effect, nuclei in hydrophobic crevices cannot be "crushed" by increasing the liquid pressure.

The rate of this evolution is highly dependent on the gradient for gas exchange, which is lowered both by the decrease of the gas pressure in the nucleus and the decrease of gas tension gradient in the liquid immediately above the gas nucleus. The evolution to interfacial radii of curvature such as -5.0 and -1.0 μm is predicted, but the determination of the times involved, t_1 and t_2 , requires a complete kinetic study.

Suppose t_1 and t_2 are the periods of pressure pretreatment. Upon return to surface, the nuclei will expand to sizes whose initial interfacial radii of curvature are negative, indicating that the nuclei have not come out of the crevice and are smaller than their original precompression sizes (Table 2). Then, upon decompression to 10.1 kPa, the nuclei expand further to interfacial radii of curvature of either negative or positive values. In Table 2 the nucleus of smaller size, i.e., with a negative value of R , was prepressurized for a longer time. Since the critical radius is 1.32 μm immediately after decompression to 10.1 kPa, there is no equilibrium state for the system and further growth will take place. However, this growth will again be limited by the two effects of gas diffusion and gas depletion discussed earlier. Thus, as the period of pressure pretreatment is increased, the period of the evolution of R toward the value of R_m is lengthened after decompression is initiated. Gas depletion in the liquid would reduce the gas tension and so, before the value of R_m is reached, the gas tension may reach a value less than 87.7 kPa, which corresponds to a critical radius of 1.5 μm ($= \omega/\sin\theta$). If so, the nucleus would not evolve out of the crevice but instead evolve toward the newly formed metastable equilibrium state. This explanation of limited growth is consistent with the decrease in the mean bubble count found in shrimp following increased periods of pressure pretreatment (9).

Pressure pretreatment with delayed decompression

A final analysis examines the effect of delaying decompression after pressure pretreatment has been applied. In the shrimp study (9), a period of 24 h at surface was imposed following 120 s of pressure pretreatment at 20.3 MPa (200 atm). The mean bubble count in the shrimp was 3.7 after decompression to 10.1 kPa. This was similar to the control case, in which no pressure pretreatment was applied (Table 1). This can be explained using the crevice model as the growth of the nucleus to its original state after pressure pretreatment is terminated. For example, in the case where the pretreatment pressure of 2.53 MPa is applied for a period t_2 , the interfacial radius of curvature of the nucleus is -3.37 μm upon return to the surface (Table 2). Since the gas tension is fixed at 98.3 kPa during the surface phase, the critical radius is infinite. This is the stable equilibrium configuration for the gas nucleus at normal surface conditions. Therefore, the nucleus will grow until its interfacial radius of curvature becomes infinite, that is, flat. The period of 24 h for the return to normal surface conditions is indicative of the rate of growth of the nucleus to its original state.

The hydrophobic crevice model has been used to demonstrate that the number of bubbles emerging from the conical crevice decreases as the period of pressure pretreatment is increased. The kinetic arguments on which this was based can also be applied to examine the effect of the magnitude of the pretreatment pressure. As the pretreatment pressure is increased, the critical radius becomes smaller while the gas pressure in the nucleus becomes larger, and the result will be an increased gradient for the transfer of gas out of the nucleus and into the liquid. Therefore, the nucleus

evolves to smaller sizes and is less likely to emerge upon decompression. This explanation is consistent with the trend of decreasing bubble appearance in the decompressed shrimp when the pretreatment pressure was increased (9).

The conical crevice model has been used to explain the stability and emergence of bubbles for the shrimp experiments. However, there are two concerns about the model. First, the height of the crevice may be unrealistically high (recall $h = 42.8 \mu\text{m}$). Second, the hydrophobic crevice condition is restrictive; that is, not all crevice walls may satisfy the hydrophobic crevice condition (i.e., $\theta > 90^\circ + \alpha$). To reduce the crevice height and to relax the hydrophobic crevice condition, another crevice geometry is introduced.

ELLIPTICAL CREVICE

At a given degree of gas supersaturation, bubbles can emerge from a hydrophobic crevice of substantially reduced height if the crevice is axisymmetric with elliptically curved walls, as shown in Fig. 3. Unlike the conical crevice, the elliptical crevice can satisfy the hydrophobic crevice condition as long as the hydrophobic surface condition is satisfied (i.e., $\theta > 90^\circ$). Unlike a narrow and shallow conical crevice, a shallow elliptical crevice provides an opening at the crevice mouth that is wide enough to facilitate bubble emergence. Also, the rounded corner of the opening of the elliptical shape is more realistic than the sharp edge of the conical shape.

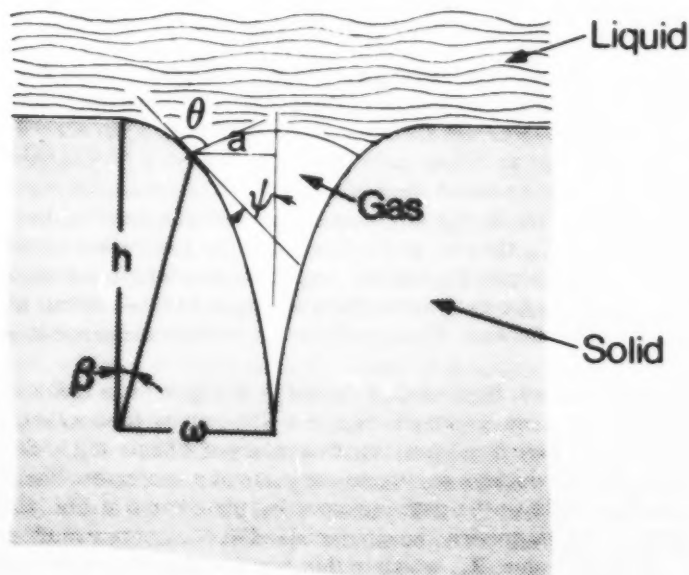


Fig. 3. Schematic of the elliptical crevice model where θ is the contact angle, h is the height of the crevice, w is the radius of the crevice mouth opening, and β is the angle measured from the vertical to the liquid-gas-solid contact point. The distance, a , and the angle, ψ , are reference values for the three-phase contact point.

The radius of curvature of the liquid-gas interface for the elliptical geometry is given by (19)

$$R = a/\cos(\theta - \psi), \quad (3)$$

where

$$a = \omega(1 - h\sin\beta/(h^2\sin^2\beta + \omega^2\cos^2\beta)^{1/2}), \quad (4)$$

and

$$\cos(\theta - \psi) = (\cos\theta + \sin\theta\tan\psi)\cos\psi, \quad (5)$$

and where ψ is defined in Fig. 3, β is the angle subtended from the vertical to the liquid-gas-solid contact point, and ω is the radius of the crevice mouth opening. The trigonometric functions in ω can be rewritten in terms of the more convenient variable, β , through the following identities:

$$\tan\psi = (\omega^2/h^2)\cot\beta, \quad (6)$$

and

$$\cos\psi = (1 + \tan^2\psi)^{-1/2}. \quad (7)$$

Therefore, the radius of curvature of the liquid-gas interface for a crevice having elliptically shaped walls can be expressed as

$$R = \omega(1 - \frac{h\sin\beta}{(h^2\sin^2\beta + \omega^2\cos^2\beta)^{1/2}}) \left(\frac{(1 + (\omega^4/h^4)\cot^2\beta)^{1/2}}{\cos\theta + (\omega^2/h^2)\sin\theta\cot\beta} \right). \quad (8)$$

A formal thermodynamic analysis for a gas nucleus in the elliptical crevice is beyond the scope of this study; however, one can make predictions on whether a gas nucleus will evolve out of the crevice on the basis of the relationship between R_m and R_c . Earlier it was noted that to assure growth of a nucleus in a hydrophobic conical crevice, R_c must be positive and of value less than R_m . It is reasonable to assume that this condition holds generally for any shaped hydrophobic crevice, since if R_c is positive and less than R_m , then it can be shown that the gas tension in the liquid is larger than the gas pressure in the nucleus, regardless of where its interface is in the crevice. Thus, a gradient for gas transfer from the liquid into the nucleus will always be present under this condition. This condition for bubble emergence is applied to the elliptical crevice.

The radius of curvature, R , is plotted against β in Fig. 4 for a radius of crevice mouth opening, $\omega = 1.5 \mu\text{m}$, a contact angle, $\theta = 91^\circ$, and for three values of crevice height, h . In Fig. 4a, where $h = 3 \mu\text{m}$, negative values of R begin at $\beta = 86.0^\circ$. Upon decompression, the gas nucleus grows and the value of β decreases. The interfacial radius of curvature follows the path indicated by the arrows in Fig. 4a. For the nucleus to grow out of the crevice, the interfacial radius of curvature must go through the positive minimum value, R_m , which in this case has the value $0.209 \mu\text{m}$ at $\beta = 82.0^\circ$. This minimum value is about an order of magnitude too small to account for the emergence of bubbles in the decompressed shrimp for a decompression ratio of 6:1 from surface ($R_c = 1.42 \mu\text{m}$, Table 1).

In Fig. 4b, where $h = 6 \mu\text{m}$, negative values of R begin at $\beta = 74.4^\circ$. The smallest positive minimum value of the interfacial radius of curvature, $R_m = 0.826$, occurs at

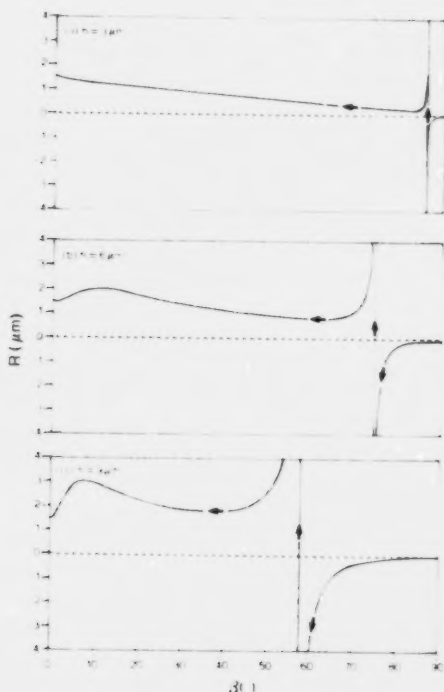


Fig. 4. Radius of curvature of the liquid-gas interface, R , for the elliptical crevice plotted against the angle β for $\omega = 1.5 \mu\text{m}$, $\theta = 91^\circ$, and for $h = 3, 6$, and $9 \mu\text{m}$. Negative values of R indicate an interface that is concave to the liquid. Arrows indicate the path of evolution of R as the gas nucleus grows out of the crevice. For the nucleus to grow out of the crevice, the interfacial radius of curvature must go through the positive minimum value of R .

$\beta = 60.5^\circ$. Note that by increasing the crevice height, a second local minimum value of R is obtained near the crevice mouth opening, $R = 1.46 \mu\text{m}$ at $\beta = 1.0^\circ$. Furthermore, by increasing the crevice height, the value of R_m is also increased, but not enough to account for bubble emergence in the decompressed shrimp for a decompression ratio of 6:1.

In Fig. 4c, where $h = 9 \mu\text{m}$, negative values of R begin at $\beta = 57.9^\circ$. In this case, the smallest positive minimum value of the interfacial radius of curvature, $R_m = 1.483 \mu\text{m}$, occurs near the crevice mouth opening at $\beta = 0.25^\circ$. A second local minimum of R , $R = 1.82 \mu\text{m}$ at $\beta = 37.6^\circ$, is obtained deeper within the crevice. Thus, by increasing the crevice height further, the barrier to bubble emergence has shifted from within the crevice to its opening. Furthermore, the value of R_m is now large enough to account for bubble emergence in the decompressed shrimp for a decompression ratio of 6:1.

In all three cases, Fig. 4a, b, and c, the interfacial radius of curvature, R , approaches a common value as β approaches zero. In fact, from eq. 8,

$$\lim_{\beta \rightarrow 0} R = \frac{w}{\sin \theta} \quad (9)$$

which represents the exact value of R_m for the conical crevice of radius of mouth opening, ω , and contact angle, θ . From the above results, this limit is approached by R_m for the elliptical crevice when the crevice height is sufficiently greater than the value of ω .

To determine the range of crevice heights for which the value of R_m for the elliptical crevice is large enough for bubble emergence, R_m is plotted against crevice height in Fig. 5 for a radius of crevice mouth opening, $\omega = 1.5 \mu\text{m}$, and for three values of the contact angle, θ . The dashed line in Fig. 5 represents the value of the critical radius ($R_c = 1.42 \mu\text{m}$) in decompressed shrimp following a decompression ratio of 6:1 from surface. Thus, crevices whose R_m values exceed $1.42 \mu\text{m}$ can account for the emergence of bubbles in these shrimp. For $\theta = 95^\circ$, this occurs for crevice heights of $3.9 \mu\text{m}$ or greater. By comparison, for the conical crevice, where $\alpha = 2^\circ$ and $\omega = 1.5 \mu\text{m}$, crevice heights must exceed $40.7 \mu\text{m}$ to satisfy the same bubble emergence condition.

For $\theta = 91^\circ$, R_m exceeds $1.42 \mu\text{m}$ for crevice heights of $7.9 \mu\text{m}$ or greater. And, for $\theta = 90.1^\circ$, R_m exceeds $1.42 \mu\text{m}$ for crevice heights of $24.8 \mu\text{m}$ or greater. Decreasing the contact angle has the effect of increasing the minimum height of the elliptical crevice to satisfy the bubble emergence condition. Note that in these last two examples, a conical crevice of $\alpha = 2^\circ$ cannot satisfy the hydrophobic crevice condition. To satisfy this condition, α must be less than $\theta - 90^\circ$. In the case of $\theta = 90.1^\circ$, to both satisfy the hydrophobic crevice condition and achieve $R_m > 1.42 \mu\text{m}$, the conical crevice height must exceed $813.6 \mu\text{m}$. Hence the elliptical crevice model gives a more realistic crevice height.

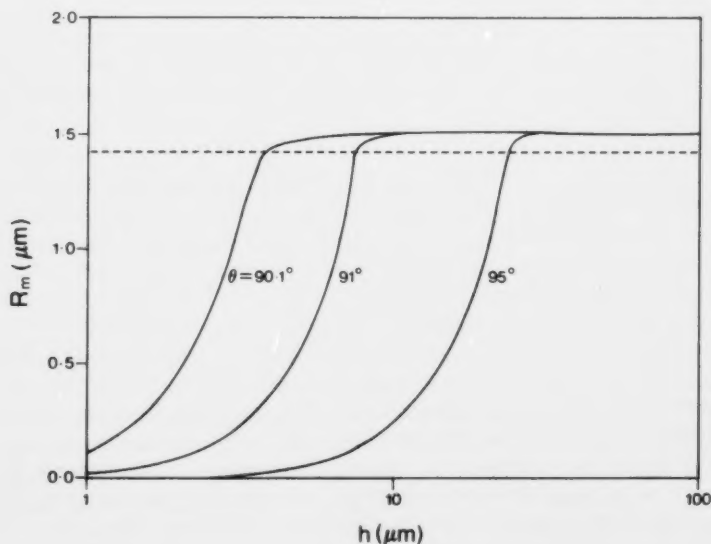


Fig. 5. Radius of minimum positive curvature of the liquid-gas interface, R_m , for the elliptical crevice plotted against the crevice height, h , for $\theta = 90.1^\circ$, 91° , and 95° . The dashed line represents the value of the critical radius ($R_c = 1.42 \mu\text{m}$) in decompressed shrimp following a decompression ratio of 6:1 from surface.

SUMMARY

The model of the hydrophobic conical crevice was used to explain the attenuating effects of pressure pretreatment on bubble formation in shrimp, the evolution of the gas nuclei to smaller stable sizes during compression, the return of the nuclei to their original stable configurations when the overpressure is removed, and the requirement for greater decompressions to cause emergence of bubbles from the nuclei as the magnitude and period of pressure pretreatment are increased. To accomplish this, the following assumptions were made: (a) a liquid surface tension of 0.060 N/m; (b) an initial total gas tension value of 98.8 kPa; (c) a contact angle of 95°; (d) a half-apex angle of 2°; and (e) a crevice height of 42.8 μm . Modification of these assumptions will result in predictions of bubble emergence different from those given here, so that a distribution of sizes could be used to explain the appearance of bubbles in the decompressed shrimp for all the decompression ratios used in the experiments of Daniels et al. (9).

To predictive qualities of the conical crevice model can be retained while the undesirable features such as large crevice height and limited range of contact angles can be lessened if the elliptical crevice geometry is used. With this more realistic shape, the height of the crevice required is reduced about an order of magnitude, and the hydrophobic crevice condition can be satisfied for any contact angle greater than 90°.

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Tikuisis P. Modèle à partir des observations sur la formation de bulles in vivo dans les crevasses hydrophobes. *Undersea Biomed Res* 1986; 13(2): 165–180.—L'hypothèse est émise que les crevasses hydrophobes in vivo dont les bulles émergent à la décompression rendraient compte des observations expérimentales de la formation des bulles dans les crevettes décompressées. Le modèle de crevasse conique peut être utilisé pour expliquer l'augmentation drastique du nombre de bulles observées dans la crevette pour des rapports de décompression supérieurs à 4:1. En accord avec les effets atténuants du pré-traitement à la pression sur la formation des bulles observées chez la crevette, le modèle peut aussi être utilisé pour expliquer: a) l'évolution des noyaux gazeux vers des granuleurs stables plus petites durant la compression; b) le retour des noyaux à leur configurations stables originales quand la surpression est enlevée; et c) la nécessité de décompressions plus grandes pour produire l'émergence de bulles des noyaux lorsque l'ampleur et la période de prétraitement à la pression est augmentée. Une nouvelle géométrie de crevasse avec des parois en forme d'ellipse est introduite, laquelle réduit la hauteur de la crevasse requise pour l'émergence des bulles et diminue les contraintes pour la stabilité des noyaux gazeux. Cette nouvelle géométrie réduit par un ordre de grandeur la hauteur des crevasses requise pour la prédiction de l'émergence des bulles comparativement à la crevasse conique, et satisfait la condition de crevasse hydrophobe en autant que la surface de la crevasse possède un angle de contact supérieur à 90°.

noyau gazeux
formation de bulles

crevasse hydrophobe
décompression

crevette

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